

Preparation of Poly(ϵ -caprolactone)/Poly(ϵ -caprolactone-co-lactide) (PCL/PLCL) Blend Filament by Melt Spinning

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ABSTRACT: Poly(ϵ -caprolactone)/poly(ϵ -caprolactone-co-lactide) (PCL/PLCL) blend filaments with various ratios of PCL and PLCL were prepared by melt spinning. The effect of PLCL content on the physical properties of the blended filament was investigated. The melt spinning of the blend was carried out and the as spun filament was subsequently subjected to drawing and heat setting process. The addition of PLCL caused significant changes in the mechanical properties of the filaments. Crystallinity of blend decreased with the addition of

PLCL as observed by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Scanning electron microscopy (SEM) revealed that the fracture surface becomes rougher at higher PLCL content. It may be proposed that PCL and PLCL show limited interaction within the blend matrix. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1944–1950, 2012

Key words: poly(ϵ -caprolactone); poly(ϵ -caprolactone-co-lactide); blend; melt spinning; biodegradable filament

INTRODUCTION

In recent years, biodegradable polymers have attracted great interests in biomedical field and a significant attention is paid toward traditional applications, such as matrices for drug delivery,^{1–3} fixation devices in orthopedic field,^{4,5} and surgical sutures.^{6,7} Moreover, biodegradable polymers may act as temporary scaffolds which can facilitate the regeneration of tissues or the cell growth in the field of tissue engineering.^{8,9}

Among biodegradable polymers, aliphatic polyesters, such as poly(lactic acid) (PLA) and poly(ϵ -caprolactone) (PCL) are very popular due to their excellent mechanical strength, biocompatibility, and bioresorbability.¹⁰ Filaments produced from synthetic poly(α -hydroxy acid), poly(L-lactide) (PLA), and poly(L-lactide-co-glycolide) [PLGA] have been investigated extensively for applications in wound repair and tissue engineering.¹¹ PLA filaments while having resorption time of around 1 year suffer from low extensibility. The PLA starting material also shows a tendency to degrade during melt processing. On the other hand, PCL filament presents a promising alternative for the production of 3D mat-

rices for use in tissue engineering. The higher compliance and extensibility of PCL relative to PLA, could present distinct advantages for regeneration of soft tissue. As a commercial material, the main attractions of PCL are (1) its biodegradability, (2) its rather unique combination of polyolefin-like mechanical properties and polyester-like hydrolysability, (3) its compatibility with a wide range of other polymers, (4) its ease of melt processing due to its high thermal stability, and (5) its relatively low cost. However, its low melting point of around 60°C and its very slow rate of biodegradation in the human body (2–3 years) have tended to restrict its use as a neat homopolymer. Consequently, PCL has been used more as a component in polymer blends or in the form of a copolymer. For example, in its biomedical applications, PCL has been blended with polymers such as cellulose propionate, cellulose acetate-butyrate, poly(lactic acid), and poly(lactic acid-co-glycolic acid) for use in long-term drug delivery systems.^{12–14} As a copolymer for suture applications, ϵ -caprolactone monomer has been copolymerized with L-lactide^{15,16} and with glycolide.^{17,18}

In the filament form, PCL has also been investigated for use in drug delivery systems,¹⁹ and also for “long-lasting” absorbable sutures.²⁰ Among PCL-based medical devices, the fibrous materials have generated considerable momentum in tissue engineering.^{21–23} This unique way of organ reconstruction offers several advantages over the conventional transplantation method as the transplant rejection is overcome and

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there is no donor requirement as cells belong to the patient himself. Several studies have been carried out to prepare filaments that have better tensile strength so that the filament retains mechanical stability initially for sufficient time during the functional use. Different spinning methods have been used by different workers for the preparation of the PCL filament, which include the melt spinning,²⁴ dry spinning,²⁵ gravity spinning,^{26,27} and wet spinning.²⁸

Owing to its ease of melt processing and its proven biocompatibility, PCL has been found to be well suited to rapid prototyping technologies such as fused deposition modeling (FDM) used in fabricating 3D scaffolds for tissue growth.⁹ Melt spinning involves heating the polymer to the required melt viscosity and subsequent extrusion as monofilament, where the filament structure and physical properties are governed by take-up speed, drawing temperature, and draw ratio.²⁹ Most of the synthetic polyester filaments used in tissue engineering are produced by a conventional melt spinning technique.³⁰

Poly(L-lactide)/Poly(ϵ -caprolactone) (PLA/PCL) blends have attracted great interest as temporary absorbable implants, but they suffer from poor mechanical properties due to the macrophase separation of the two immiscible components and to the poor adhesion between the phases.³¹ Since PLA with a high molecular weight is usually immiscible with PCL even at molten temperatures, the morphology of PLA/PCL blend becomes coarse and the adhesion strength becomes poor; thus, desirable mechanical properties are not anticipated.^{32,33} The objective of this study is to prepare PCL/PLCL blended filament which can be used for biomedical applications. The beauty of this system is that this is a completely biodegradable system and may be used for the internal surgery in human beings. The influence of processing conditions and the PLCL content on the physical properties of the filaments is investigated.

MATERIALS AND METHODS

The poly(ϵ -caprolactone) (PCL) was a commercial product (Aldrich Chemical, Product No. 44,074-4) with a stated number-average molecular weight, M_n , of $\sim 80,000 \text{ g mol}^{-1}$ (gel permeation chromatography (GPC)). It was supplied in the form of white beads which were stored in a vacuum before use. Poly(ϵ -caprolactone-co-lactide) (50 : 50) (PLCL) was received from Polymer laboratory, University of Uppsala, Sweden and was stored under vacuum at ambient conditions.

Intrinsic viscosity measurement

The viscosity of PCL and PLCL was measured in chloroform using Ubbelohde viscometer in a

constant temperature bath at a temperature of 25°C. The intrinsic viscosity was determined from the flow behavior of the solutions of different concentrations and the viscosity average molecular weight was calculated from the following equation.

$$\eta = K M_v^\alpha$$

where η is the intrinsic viscosity, M_v is the viscosity average molecular weight, K and α are the constants. The value of K and α was 1.25×10^{-4} and 0.82, respectively, for PCL.³⁴

Preparation of blend

Binary blends of PCL with PLCL were prepared by dissolution of PCL and PLCL in chloroform solution. The blends composition ranged from pure PCL to a composition of PCL : PLCL, 90 : 10, 80 : 20, 70 : 30, 60 : 40, and 50 : 50. For blend preparation, PLCL was dissolved in chloroform and allowed to swell for 6 h. The PCL was subsequently added and the solution was stirred to get a homogeneous mixture. The mixture was poured in a petri dish and dried under vacuum for 16 h at 100°C. The blend formed was subsequently spun into filaments by melt spinning.

Spinning

Dried PCL/PLCL blend was subsequently compressed into cylindrical rods. This was done by warming the blend in the cylinder end capped with a plain blanking plate under pressure from the ram. A temperature of 60°C was found to be suitable for this purpose, just enough for the blend to soften without appreciable melting under nitrogen. The melt spinning of the blend was done at a spinning temperature of 180°C under nitrogen atmosphere.

Drawing

The as-spun filament was subjected to drawing and heat setting operations. The filament was drawn at the drawing temperature of 30°C, followed by the heat setting at 30°C under tension conditions.

Diameter measurement

The diameter of all the samples was measured using Light microscope photographs taken by a JVC TK-C1380E digital color video camera attached to a Leica DMLP polarized light microscope. Five values were averaged out to get the final reading for each sample.

TABLE I
The Polymers Used in the Study and the Blend
Composition Prepared with the Diameter of Filaments

Polymer/Composition	Code	Diameter of filament (μm)
Poly(ϵ -caprolactone)	PCL	128 ± 1.8
Poly(ϵ -caprolactone- <i>co</i> -lactide) (50 : 50)	PLCL	–
PCL/PLCL (90 : 10)	PCL90	126 ± 4.1
PCL/PLCL (80 : 20)	PCL80	133 ± 3.1
PCL/PLCL (70 : 30)	PCL70	118 ± 3.2
PCL/PLCL (60 : 40)	PCL60	138 ± 2.5
PCL/PLCL (50 : 50)	PCL50	122 ± 6.5

Mechanical properties

The tensile properties of PCL/PLCL blend filaments were measured using a Tinius Olson tester. All the experiments were carried out using gauge length of 50 mm and rate of testing as 150 mm/min. Tensile strength and elongation at break of the filaments were determined from the stress–strain curve.

X-ray diffraction

X-ray diffraction (XRD) patterns of the PCL/PLCL blend filaments were recorded in the 2θ range of 5° to 40° on a Phillips X-ray diffractometer equipped with a scintillation counter. $\text{CuK}\alpha$ radiation (wavelength, 1.54 \AA) was used for X-ray diffraction experiments.

Differential scanning calorimetry (DSC)

DSC studies on filaments were carried out on Perkin–Elmer DSC-7 system. Vacuum-dried samples were loaded and the thermograms were run in the temperature range of -50 to 100°C under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The melting enthalpy (ΔH_f) values were obtained from the area under the melting thermograms. The crystallinity was obtained by the following expression:

$$\text{Crystallinity}(\%) = \frac{\Delta H_f}{\Delta H_{f(\text{cryst})}} \times 100$$

where ΔH_f is the melting enthalpy of the sample and $\Delta H_{f(\text{cryst})}$ is the melting enthalpy of 100% crystalline PCL and was taken as 139.5 J/g .³⁵

Thermogravimetric analysis (TGA)

TGA was carried out using Perkin–Elmer TGA-7. The tests were carried out in nitrogen atmosphere for the temperature range of 50 – 600°C with the heating rate $10^\circ\text{C}/\text{min}$.

Scanning electron microscopy

The phase morphologies of the PCL/PLCL blends were investigated by SEM. The filaments were immersed in liquid nitrogen and then fractured to prepare the samples for SEM. The phase morphologies of filaments were studied using a CARL ZEISS EVO 50, scanning electron microscope, after coating them with silver.

RESULTS AND DISCUSSION

The blend compositions and their code along with the diameter of the filaments are presented in Table I. The intrinsic viscosity (IV) of the PCL and PLCL were found to be 1.5 dL/g and 0.63 dL/g , respectively. DSC heating curves for the filaments of different compositions are presented in Figure 1. The DSC thermogram of PCL shows a sharp endothermic peak at 60.2°C corresponding to melting transition. This is in agreement with the previous workers.^{36,37} PLCL, on the other hand does not show any transition corresponding to its amorphous nature. The addition of PLCL to the PCL causes broadening of the melting peak of the PCL and a shoulder formation with the increasing PLCL content. This can be attributed to the melting of two different types of crystals which may be due to two groups of structures in the crystalline phase.³⁸ However, no significant shift in the endothermic peak is observed representing the melting of PCL by blending PCL with PLCL. The melting peak of PCL occurred at 60.3°C in PCL50 as well. The compositional dependence of T_m of the blends is shown in Figure 2. Addition of PLCL to PCL does not cause any significant change in the melting point of the

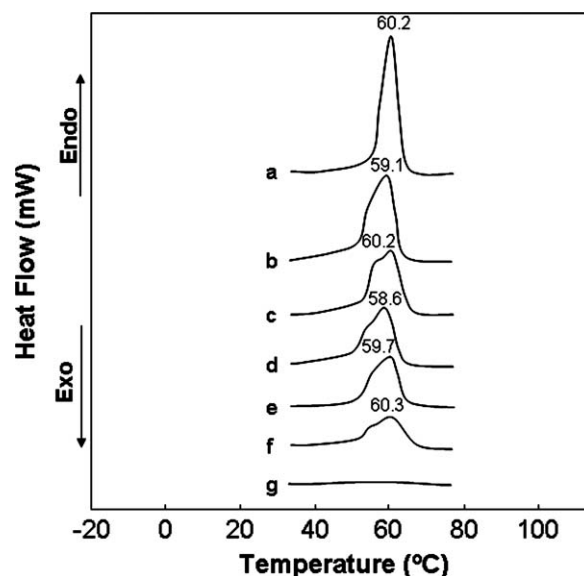


Figure 1 DSC Heating curves of filaments of different blend compositions (a) PCL, (b) PCL90, (c) PCL80, (d) PCL70, (e) PCL60, (f) PCL50, and (g) PLCL.

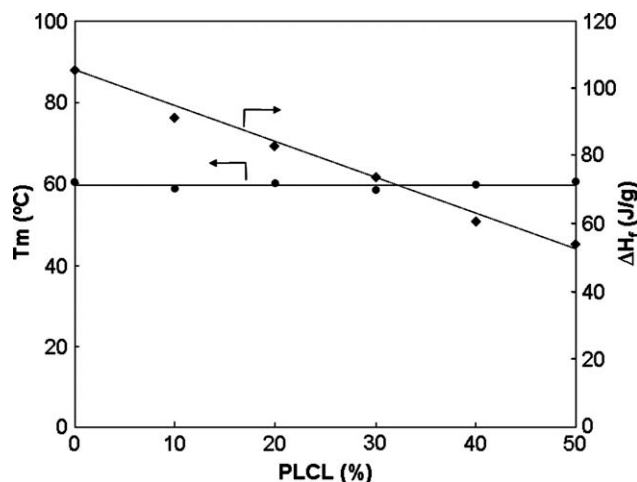


Figure 2 Variation of the melting temperature and heat of fusion with the PLCL content.

blend for the whole range of PLCL content. The above results indicated that the interaction between the two polymers does not cause any change in the inherent crystalline phase of the PCL. The area of the melting peak and hence the heat of fusion decreases with the increase in the concentration of PLCL in the blend showing decrease in the crystallinity with the addition of PLCL. Looking at the amorphous nature of PLCL component, it is expected that the addition of PLCL to the PCL enforces the dilution of the inherent crystallinity and would follow the trend represented by the dotted line which represents the theoretical heat of fusion values (ΔH_f). The heat of fusion values of the blends falls on this dotted line (as shown in Fig. 2), ascertaining that the inherent crystallinity of PCL remain intact and the decrease is solely due to the incorporation of amorphous PLCL into the noncrystalline region of PCL.

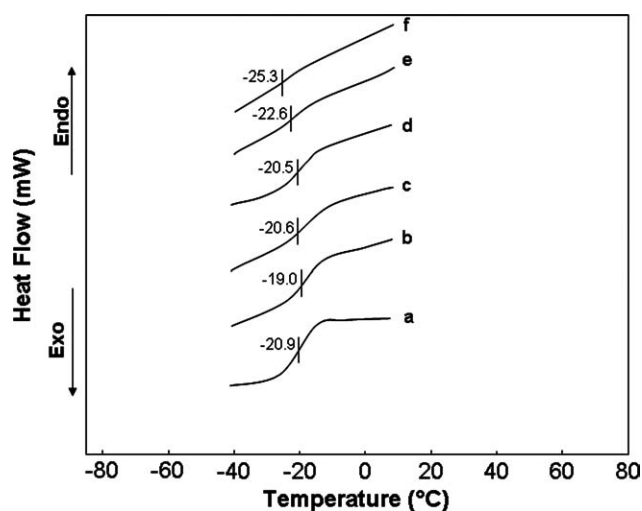


Figure 3 DSC thermograms of filaments of different blend compositions (a) PLCL, (b) PCL50, (c) PCL60, (d) PCL70, (e) PCL80, and (f) PCL90.

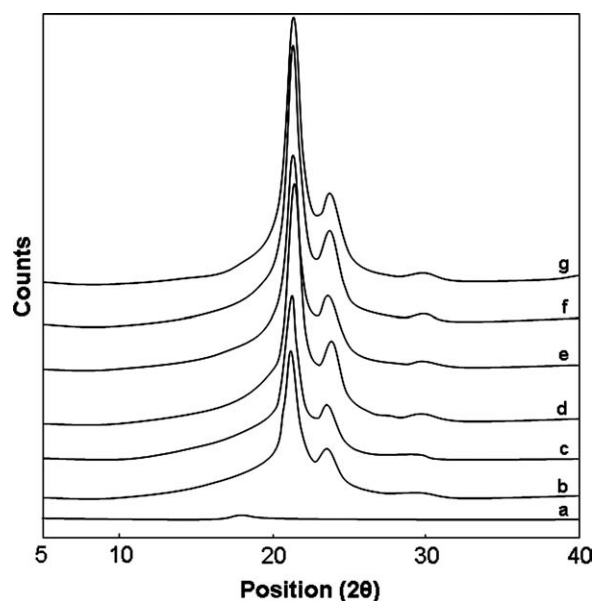


Figure 4 X-ray diffraction patterns of the filaments of different blend compositions (a) PLCL, (b) PCL50, (c) PCL60, (d) PCL70, (e) PCL80, (f) PCL90, and (g) PCL.

One of the most utilized criteria to determine the miscibility or phase separation of a polymer pair is that of the glass transition temperature (T_g). In miscible blends, an intimate mixture occurs at molecular level and therefore a single T_g is observed at an intermediate temperature of the pure components. On the other hand, when polymer blends exhibit two separate T_g s at the same position of the pure components, an immiscible system is envisaged. No shift in T_g of PLCL was observed on blending PCL with PLCL (Fig. 3). The T_g of pure PLCL was -20.9°C and the T_g of PLCL in the blend was observed in the range of -19.0°C to 25.3°C . Therefore, it can be concluded that the PCL/PLCL blend system is partially miscible system with each other.

The X-ray diffraction pattern of the filaments is presented in Figure 4. XRD of PCL shows two characteristic peaks at 21° and 23° 2θ . All diffractions lie at identical angles, and no additional diffraction peaks were visible in the blended filaments, indicating that the crystalline phase does not change during blending process. The intensity of all the peaks decreases with the increase in the concentration of PLCL, showing decrease in the crystallinity with the addition of PLCL. Variation of percent crystallinity with the composition of the blend as measured from XRD is shown in Figure 5. The dependence of the crystalline content on composition was approximately linear. Thus, the crystalline content of the neat PCL remained almost constant in its blends. This decrease in the crystallization ability of PCL in the presence of PLCL suggests that interactions between the blend components are not strong. The crystallinity of the blend decreases linearly with the

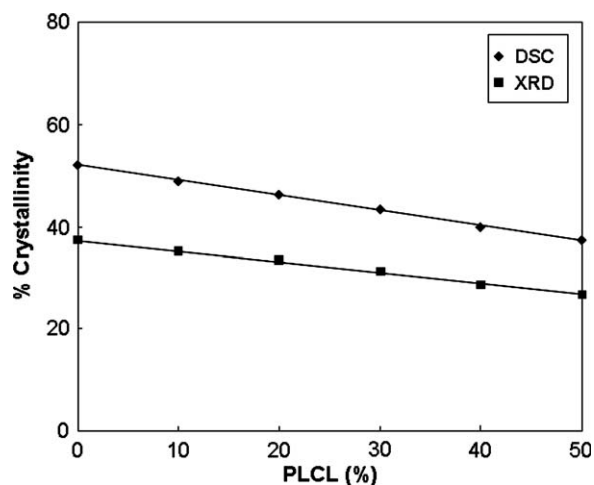


Figure 5 Variation of the percent crystallinity with PLCL content as measured from DSC and X-ray diffraction.

increase in the concentration of PLCL. This is because in this blend the PCL is the only crystalline part and the PLCL is the amorphous part. This suggests that the addition of amorphous PLCL causes decrease in the crystallinity of the blend. The same trend of decrease in crystallinity with the increase in the concentration of PLCL in the blend was observed by DSC also (Fig. 5). The crystallinity value obtained by DSC was greater than the crystallinity obtained by the XRD for the same sample. This is because the sample tends to crystallize during heating in DSC.

Figure 6 shows the stress–strain curve of the filaments with different compositions of PCL/PLCL. PCL shows a linear slope at low deformations before yielding and a ductile behavior, according to its rubbery state at room temperature. The tensile curves of PCL/PLCL blends reveal inferior strength, and ductility when compared with the pure PCL. Figure 7

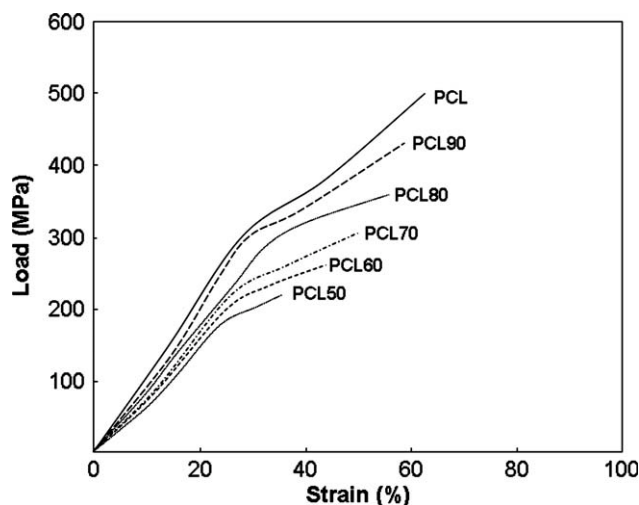


Figure 6 Stress–strain plot of filaments of different blend compositions.

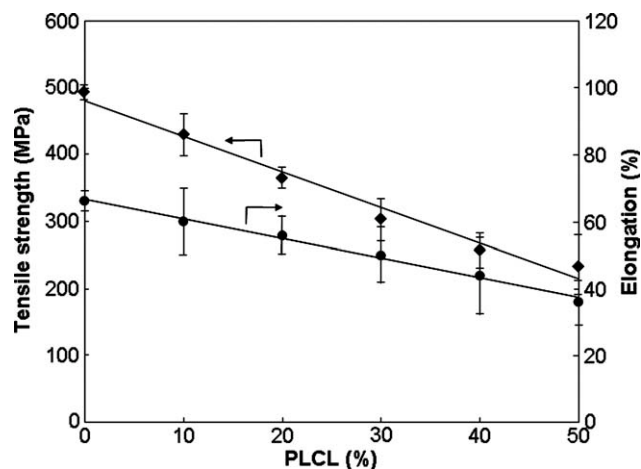


Figure 7 Variation of tensile strength and elongation with PLCL content.

shows the variation of the tensile strength with the PLCL composition. Tensile strength decreases with the increase in PLCL concentration in the blend. The tensile strength of pure PCL filaments was 493 MPa compared with the 234 MPa of PCL50. The initial modulus also follows similar pattern as that of tensile strength (Fig. 8). The decrease in tensile strength with increasing concentration of PLCL shows that PLCL act as non-reinforcing component. Variation of elongation of the filament with composition of the blend is shown in Figure 7. Elongation decreases from 66% of PCL to 36% of PCL50, with the increasing concentration of PLCL in the blend. In synthetic blends with a ductile matrix, the elongation at break is considered to be highly sensitive to the state of the interface. The reduction in the elongation at break in the blend with increasing concentration of PLCL can be due to the limited interaction between PCL and PLCL. Similar results of reduction in elongation was observed in case of PCL and starch blend by Rosa et al.³⁹

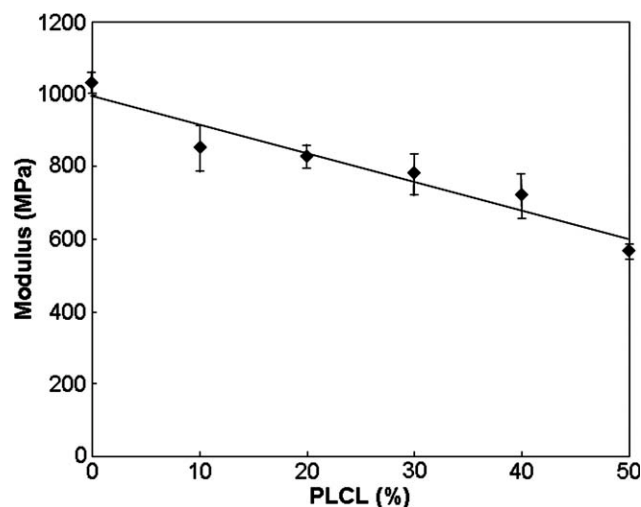


Figure 8 Variation of initial modulus with PLCL content.

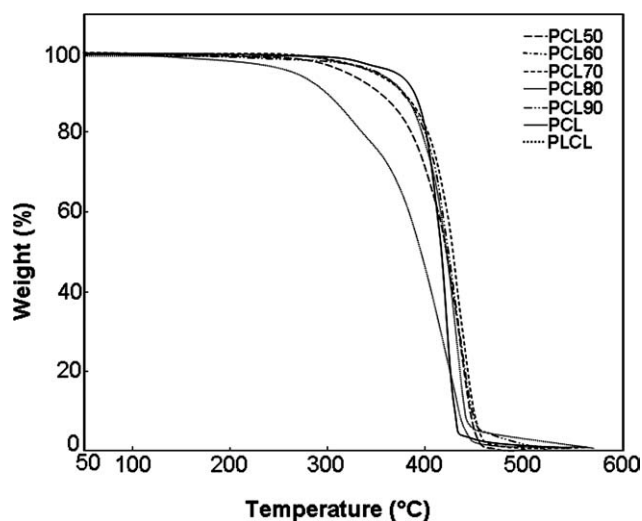


Figure 9 TGA thermograms of the PCL/PLCL blend filament.

The TGA profiles of PCL, PLCL, and their blends are shown in Figure 9. PCL degrades in a single stage (around 300°C) involving simultaneous occurrence of two types of reactions *viz*, random chain scission and unzipping from hydroxyl end leading to the formation of ϵ -caprolactone.^{40,41} TGA of PLCL showed weight loss starting around 243°C and suggested faster thermal degradation of the polymer. PCL on the other hand, showed more stable thermo-

gram where weight loss starts at 297°C. Looking at the chemical nature, PLCL and PCL are both aliphatic polyesters with a fairly close thermal expansion coefficients and difference in solubility parameters. However, due to low molecular weight, PLCL undergoes faster chain fragmentation when compared with PCL which is of higher molecular weight when compared with PLCL. TGA of all the blend composition showed weight loss in single step. Initial degradation temperature (IDT) of pure PCL and PLCL are 297°C and 243°C, respectively. The IDT for all blend compositions fall between the two pure components, i.e., PCL and PLCL. This is reasonably in agreement with the lower PLCL thermal stability influencing the degradation behavior of blend.

The filaments were immersed in liquid nitrogen and then fractured, and then the fractured surfaces were analyzed using SEM. SEM micrographs of cryo-fractured surfaces of these blends are shown in Figure 10. The fractured surface of PCL was homogenous and SEM images indicate fine blend morphologies with dispersed phase domains. The fractured surface becomes rougher with increasing PLCL concentration. The two components, i.e., PCL and PLCL seems to be interacting with each other and do not show any phase separation at least for low level (up to 30%) of PLCL in the blend. Thereafter, the PLCL component tends to make its own domains and is reflected in the form of distinct morphology. Fine

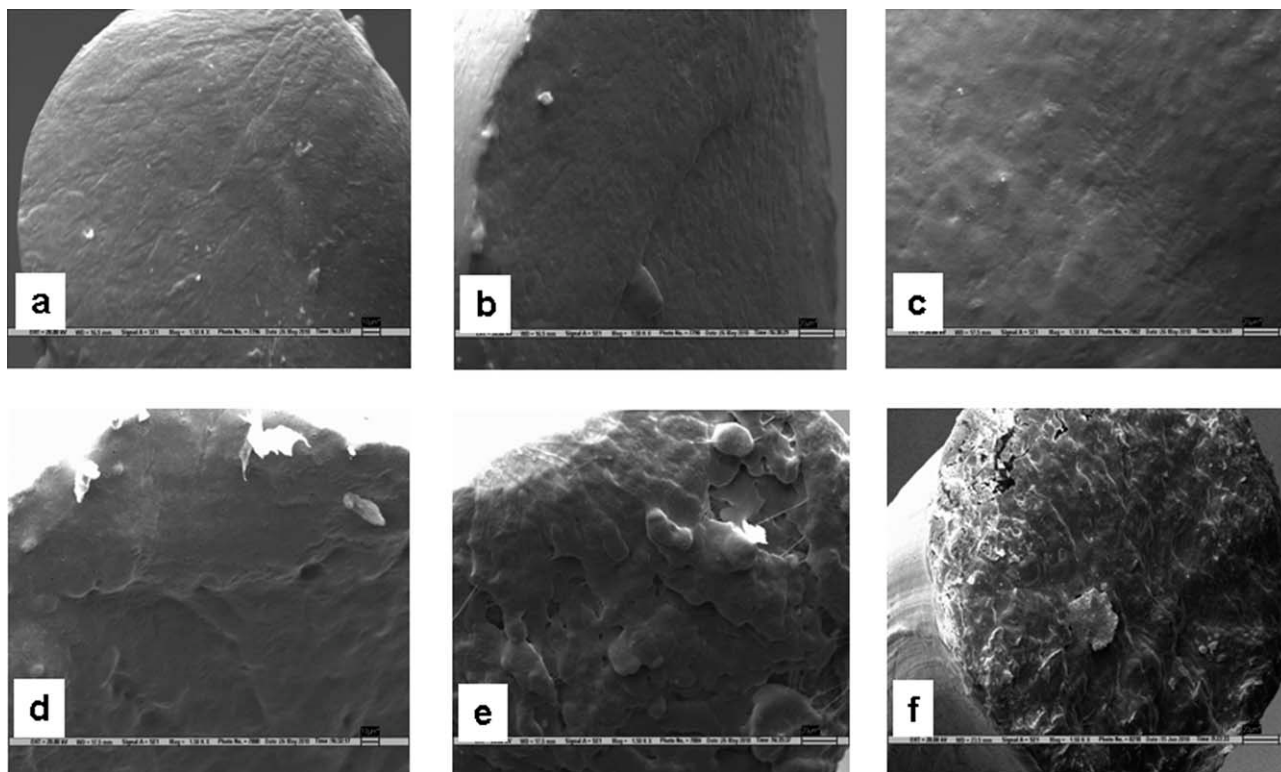


Figure 10 SEM images of fractured surfaces of the blended filaments (a) PCL, (b) PCL90, (c) PCL80, (d) PCL70, (e) PCL60, and (f) PCL50.

morphology of blend was attributed to the presence of PCL in two phases of the blends by Granado et al.⁴²

CONCLUSIONS

PCL/PLCL-blended filaments were prepared by melt spinning process. The thermal stability was not altered significantly on blending PCL with PLCL as revealed by the TGA analysis. Since all blend compositions were thermally stable well above 300°C, therefore melt spinning can be used to produce filament from various compositions. The addition of PLCL caused significant decrease in the mechanical properties of the filaments. Both the modulus and elongation diminished significantly. The crystallinity of the blend decreases linearly with the increase in the concentration of PLCL. This is due to the dilution of inherent crystallinity of PCL by the addition of amorphous PLCL moiety. Certainly, the PLCL component neither forms independent domains within the blended matrix nor offers any reinforcing effect on the filament structure. On this basis, it is reasonable to assume that limited interactions are obtained in binary PCL/PLCL blends because of the similar chemical nature of the blend components. SEM showed that the two components, i.e., PCL and PLCL seems to be quite compatible with each other and do not show any phase separation at least for low level (up to 30%) of PLCL in the blend. Beyond 30% PLCL content, the SEM studies reveal the appearance of microdomains within the blended matrix and show that the incompatibility between the components arises for higher content.

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